Urban Stormwater Runoff Aquatic Life Toxicity: An Update

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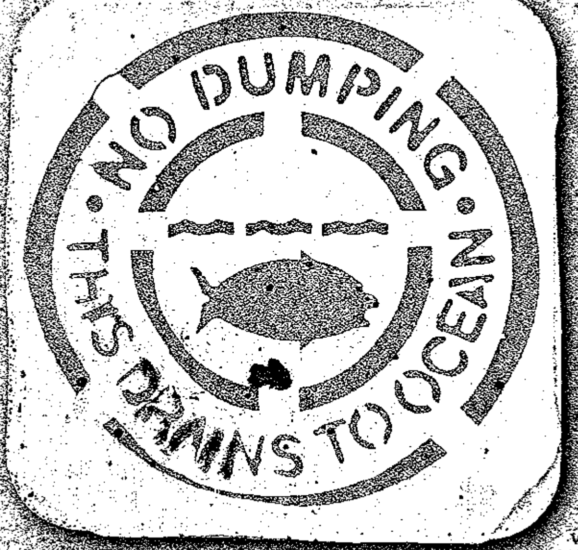
REGULATING PESTICIDES



The January/February 2001 issue of *Stormwater* contained the article "The Urban Pesticide Problem" (http://stormh2o.com/sw_0101_urban.html), in which we discussed that urban stormwater runoff was toxic to *Ceriodaphnia dubia*, as shown using an EPA (2002) standard test zooplankton for assessing aquatic life toxicity in fresh water. This toxicity is a violation of the Clean Water Act and, in California, of the Regional Water Quality Control Board Basin Plan objective for controlling aquatic life toxicity. Toxicity investigation evaluations (TIEs) showed that the urban stormwater runoff–associated toxicity was primarily due to the organophosphorus (OP) pesticides diazinon and chlorpyrifos used on residential properties. This article presents a review of the current situation with respect to pesticide-caused aquatic life toxicity in urban stormwater runoff now that the EPA no longer allows the sale of diazinon and chlorpyrifos for urban residential use. The restriction on sale for residential use was not based on aquatic life toxicity but on the potential cumulative impact to children under the Food Quality Protection Act.

OP Pesticide TMDLs

In the mid-1990s, several California Regional Water Quality Control Boards placed urban streams on the Clean Water Act 303(d) list of impaired water bodies because of the OP pesticide-caused aquatic life toxicity. At this time, several of the Regional Boards are adopting total maximum daily loads (TMDLs) to control aquatic life toxicity in urban streams caused by diazinon and chlorpyrifos, even though the sale for the use of these pesticides on residential properties and for most urban uses has been terminated. There are, however, still some urban uses allowed, and there is the potential for the allowed uses of these pesticides on agricultural lands to cause aquatic life toxicity in urban areas.

Some of the Regional Boards' TMDLs are available online (see sidebar).

We have prepared a report for developing a TMDL for diazinon- and chlorpyrifos-caused aquatic life toxicity in several Stockton, CA, sloughs (Lee and Jones-Lee 2002). As discussed in this and other urban TMDL reports, the TMDL target for control of OP pesticide-caused aquatic life toxicity is typically set at the water-quality criterion for diazinon and chlorpyrifos. The California Department of Fish and Game (CDFG) recalculated acute water-quality criterion for diazinon is 160 nanograms per liter. The CDFG diazinon chronic criterion four-day average is established as 100 nanograms per liter.

A National Problem

Based on the US Geological Survey report (Larson, Gilliom, and Capel 1999) covering the USGS national pesticide monitoring program, there are sufficient concentrations of diazinon and chlorpyrifos in urban streams located in several areas of the US to be toxic to *Ceriodaphnia*. We have stated that "it is now clear that the aquatic life toxicity problem associated with the use of OP pesticides on residential properties is a largely unrecognized national problem that needs attention" (Lee and Jones-Lee 2002). TDC (2003) has provided a more recent discussion of recent USGS data on pesticide concentration in US waters. In the early 1990s, many US waters in urban and agricultural areas contained sufficient OP pesticides to cause aquatic life toxicity.

Pesticide Regulatory Process

The termination of the sale of diazinon and chlorpyrifos for essentially all urban uses has caused the substitution of other pesticides for use on residential properties. It might be assumed that the substitution of a pesticide for residential use would be regulated to ensure that the replacement pesticide does not cause aquatic life toxicity in stormwater and fugitive water runoff. However, the EPA Office of Pesticide Programs (OPP's) registration of pesticides for urban and agriculture use does not prevent the use of pesticides in accord with the registration label, although they can be present in urban and agricultural stormwater runoff and discharges and are highly toxic to aquatic life in the receiving waters for the runoff.

Another complicating factor in regulating the pesticide-caused aquatic life toxicity is the different regulatory approaches that are used for controlling pesticide impacts on non-target organisms versus the control of toxicity to aquatic life. The Clean Water Act as being implemented by the EPA requires the control of toxics discharged in toxic amounts. Pesticides are regulated by the EPA Office of Pesticide Programs. The EPA OPP Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) regulations allow toxicity to non-target organisms provided that this toxicity is not significantly adverse to the beneficial uses of the water body. FIFRA definitions include:

x) Protect health and the environment — The terms "protect health and the environment" and "protection of health and the environment"' mean protection against any unreasonable adverse effects on the environment.

3 (bb) Unreasonable Adverse Effects on the Environment — The term 'unreasonable adverse effects on the environment' means (1) any unreasonable risk to man or the environment, taking into account the economic, social, and environmental costs and benefits of the use of any pesticide, or (2) ...

The FIFRA regulations allow other factors (such as economic and social) than impairment of beneficial uses of a water body to determine whether a pesticide's registration or re-registration should be limited by adverse impacts to non-target organisms. The FIFRA regulations point to the need to have a much better understanding of the role of specific types of zooplankton that are impacted by OP pesticide toxicity in influencing beneficial uses of water bodies. Basically, from an OPP perspective, the question becomes one of whether the numbers, types, and characteristics of aquatic life present in receiving waters for urban stormwater runoff containing OP pesticide-caused aquatic life toxicity are being significantly adversely impacted by this toxicity while the Clean Water Act prevents all aquatic life toxicity.

There is no regulatory proactive process whereby a new or substitute pesticide is critically reviewed for stormwater runoff water-quality impacts before widespread use can take place. It was based on this situation that we recommended the water-quality regulatory agencies adopt a proactive approach of requiring stormwater runoff water-quality impact studies to be conducted with the initial use of a new- or expanded-use pesticide (Jones-Lee and Lee 2000b; Lee 2001). The results of these studies could be used to screen for aquatic life toxicity problems in stormwater runoff from areas where the pesticides are initially applied before widespread application occurs.

Development of an Approach for Evaluating Potential Pesticide-Caused Toxicity. The TMDLs that are being adopted by the California Regional Water Quality Control Boards do not require an evaluation of potential aquatic life toxicity of replacement pesticides for diazinon and chlorpyrifos be conducted. However, the Regional Boards are incorporating toxicity monitoring requirements into the National Pollutant Discharge Elimination System (NPDES) permits for urban stormwater management agencies. The previously required monitoring of the stormwater runoff has been expanded to include receiving water water-column monitoring. As an example, the City of Sacramento, CA, NPDES permit is available online (see sidebar).

A problem with the Central Valley Regional Water Quality Control Board monitoring program for stormwater runoff is that no monitoring is required for sediment toxicity. This is an especially significant deficiency because the pyrethroid-based pesticides now being sold as replacement for the OP pesticides accumulate in the urban stream sediments where there is a potential to cause aquatic life toxicity.

Potential Problems With Pyrethroid Pesticides. Reviews of the pesticides that are marketed for home use as replacements for diazinon and chlorpyrifos have shown that several of the pyrethroid-based pesticides are being used for this purpose. Several of these pesticides are as toxic, if not more toxic, to zooplankton than diazinon and chlorpyrifos. Further, they are more toxic to fish. The pyrethroid-based pesticides tend to have much stronger sorption tendencies and therefore become attached to surfaces to a greater degree than the OP-based pesticides. Some manufactures of pyrethroid-based pesticides have claimed that these stronger tendencies would eliminate the problems of stormwater runoff–caused aquatic life toxicity associated with OP pesticides. However, pyrethroid-based pesticides used in agricultural areas are being found by Weston, You, and Lydy (2004) in receiving water sediments for stormwater runoff/discharges from areas where they are being applied in California's Central Valley water bodies. This could be occurring in urban stream sediments as well, although there are no known data showing this. The Weston, You, and Lydy (2004) studies include finding that the sediments where pyrethroid-based pesticides are being found are toxic to some benthic organisms. The measuring of these pesticides was based on solvent extraction that recovered all pyrethroid-based pesticides in the sediment sample. As yet, however, it has not been shown that this toxicity is due to the presence of the pyrethroid pesticide in the sediments. It is known that the sorption of pesticides and some other chemicals eliminates the toxicity to many types of aquatic life. Ankley et al. (1994) reported that the sorption of chlorpyrifos on total organic carbon resulted in its detoxification. However, apparently there are some filter feeders that can be impacted by sorbed particulate pesticides through ingestion of the particles that contain the sorbed pesticide.

A significant problem exists in trying to work with the pyrethroid-based pesticides in that their strong sorption tendencies make conducting TIEs on sediment and water samples difficult at this time. Under these conditions, a standard additions approach is used, in which a small amount of the pyrethroid pesticide that is present in a toxic sediment sample is added to the sample to see if the toxicity increases proportionally to the amount added. If it does not, then the toxicity is not likely due to the pyrethroid pesticide, but to some other substance.

Lee and Taylor (2001) in their late-1990s studies of aquatic life toxicity in the stormwater runoff in the Upper Newport Bay Orange County, CA, watershed found evidence for pyrethroid toxicity based on piperonyl butoxide (PBO) activation of the toxicity in water samples. At that time, about 25,000 pounds (ai) of pyrethroid-based pesticides were being used each year on agriculture in Orange County. The PBO activation is an indication that pyrethroid-based pesticides could be present in the sample. However, it was not possible to confirm that part of the

For More Information Online

Regional Water Board TMDLs

San Francisco Regional Water Quality Control Board TMDL for OP pesticide-caused aquatic life toxicity

www.swrcb.ca.gov/rwqcb2/urbancrksdiazinontmdl.htm

Central Valley Regional Water Quality Control Board TMDL for controlling OP pesticide-caused aquatic life toxicity in the greater Sacramento, CA, area

www.swrcb.ca.gov/~rwqcb5/programs/tmdl/urbancreeks/urbancrksreport.pdf

Santa Ana Regional Water Quality Control Board TMDL for diazinon and chlorpyrifos: **www.waterboards.ca.gov/santaana**

San Diego Regional Water Quality Control Board TMDL for diazinon and chlorpyrifos: **www.waterboards.ca.gov/sandiego**

City of Sacramento NPDES Permit

www.swrcb.ca.gov/~rwqcb5/adopted_orders/Sacramento/R5-2002-0206.pdf

Alternatives to Chlorpyrifos (EPA)

www.epa.gov/pesticides/op/chlorpyrifos/alternatives.htm

Urban Pesticide Committee

www.swrcb.ca.gov/rwqcb2/urbancrksdiazinontmdl.htm

toxicity that Lee and Taylor found in the Upper Newport Bay watershed stormwater runoff was due to pyrethroid-based pesticides.

At this time it is still unclear whether the use of pyrethroid-based pesticides in urban and agricultural areas is causing aquatic life toxicity, especially to benthic organisms. There is a need to determine whether the current use of pyrethroid-based pesticides is causing water-quality problems in aquatic systems, with particular reference to sediment toxicity.

New- or Expanded-Use Pesticides in Urban Areas. In an effort to learn more about the types of pesticides being used as replacements for diazinon and chlorpyrifos in urban areas, the San Francisco Regional Water Quality Control Board funded the TDC Environmental Report: Insecticide Market Trends and Potential Water Quality Implications (TDC 2003). This report contains information on urban pesticide use in the San Francisco Bay Area as of 2002 and in California based on Department of Pesticide Regulation (DPR) 2000 pesticide use reporting.

Neonicotinoid Pesticides. Zalom, Toscano, and Byrne (2005) discuss some of the issues associated with the replacement of OP pesticides diazinon and chlorpyrifos with pyrethroid and neonicotinoid-type pesticides. The neonicotinoid pesticides are synthetic chemicals based on the structure of nicotine. The article mentions that several of the neonicotinoid-type pesticides are being used in substantial amounts in California agriculture. For example, in 2002, 6,632 pounds (ai) of acetacioprid, 224,730 pounds (ai) of imidacloprid, and 11,091 pounds (ai) of thiamethoxam were used. According to Zalom, Toscano, and Byrne, the primary use is on fruits and vegetables: "The neonicotinoids are a new class of pesticides that are now being realized."

The EPA's Web site shows "Alternatives to Chlorpyrifos," listing imadacloprid for home lawn and ornamental products, among other uses (see sidebar). The DPR (2005) has reported that 148,553 pounds (ai) of imidacloprid were used in California in 2003. Most of this use was on vegetables and fruits, with 16,765 pounds (ai) used on landscape maintenance and 46,528 pounds (ai) used for "Structural Pesticide Control." The DPR pesticide-use database includes only application by agriculture and in urban areas by commercial pest control applicators. It does not include the amounts purchased by the public in garden supply stores. For the OP pesticides, it was estimated that as much diazinon and chlorpyrifos was used by the public on residential properties as by commercial applicators.

A visit to a home and garden supply store in Davis, CA (population about 50,000), shows that Bayer Environmental Services is selling several products for home outdoor use that contain imidacloprid including a granular product that is to be applied to lawns by a spreader for grubs. Another Bayer product is being sold in a hand spray bottle that contains imidacloprid for use on "rose and flower." This product also contained the pyrethroid cyfluthrin.

The use of imidacloprid on residential properties raises questions about whether this pesticide could cause aquatic life toxicity in stormwater and fugitive water runoff. Zalom, Toscano, and Byrne (2005) have indicated that the "neonicotinoids are more similar to the OPs than pyrethroids in their potential to move through soil and runoff in surface waters." They also state that "imidacloprid is soluble in water (5.14 g/L), has moderate binding capacity to organic materials in soils (K_{OC} = 262) and a relatively long half-life in soils (365 days)."

A review of the EPA OPP Ecotoxicity Database shows imidacloprid has LC50 for several types of freshwater and marine fish and *Daphnia magna* in the order of 100 milligrams per liter. The most sensitive aquatic organism tested in registration of the pesticides with EPA OPP was mysid with a LC50 of about 4,000 nanograms per liter. In comparison the diazinon LC50 for *Ceriodaphnia dubia* is about 400 nanograms per liter and for *Daphnia magna* is about 1,000 nanograms per liter. Based on the studies of Lee and Taylor (2001) in the Upper Newport Bay watershed where several OP and carbamate pesticides were found in stormwater runoff, pesticides with LC50 values above about 3,000 nanograms per liter that are applied in a manner similar to diazinon, and with similar mobility, would rarely cause receiving water toxicity to larval fish, zooplankton like *Ceriodaphnia*, and green algae. Marshall Lee of the California DPR and Jeff Miller of AquaScience in Davis, CA, have indicated in personal communications that they agree with this assessment. According to the EPA OPP Web site information on neonicotinoids, the rates of application tend to be less than for many other pesticides.

Marshall Lee (personal communication, 2005) has pointed out that there are exceptions to this guideline where some pesticides are toxic to some fish at very low concentrations well below the LC50. He cites as an example the toxicity of molinate to carp The LC50 for molinate to carp is about 100 micrograms per liter; however much lower concentrations affect carp by inhibiting blood clotting This type of pesticide and fish species–specific toxicity should be considered when evaluating the potential impact of a pesticide to aquatic life.

From this preliminary assessment it appears that the use of imidacloprid for home use as a replacement for chlorpyrifos and diazinon would not likely be a cause of stormwater runoff aquatic life toxicity However, as discussed by Zalom, Toscano, and Byrne (2005), there is concern that imidacolprid has the potential to cause groundwater pollution: Neonicotinoids are more similar to OPs than pyrethroids in their potential to move through the soil and run off in surface water The California Pesticide Contamination Prevention Act of 1985 established a set of specific numerical values (SNVs) for pesticides and required the DPR to place active ingredients on a list of candidates as potential leachers if their water-solubility value exceeds 3 parts per million or if the soil adsorption coefficient is less than 1,900 cubic centimeters per gram, and if one of three persistence parameters is exceeded. The three major neonicotinoids currently registered in California all exceed the SNVs and are on the list, suggesting that care is needed when using these products to protect water quality.

The DPR (2004a, b) in accord with Section 13145(d) of the Food and Agricultural Code has listed imidacloprid as having the potential to move to groundwater However, the use of imidacloprid currently does not require a groundwater protection permit In accordance with current DPR regulations, before a pesticide is listed as requiring a groundwater protection permit, it must have been found to have caused groundwater pollution This approach is not protective of groundwater quality because, based on the properties of a pesticide and soil aquifer characteristics, it is possible to predict whether a pesticide will likely cause groundwater pollution The potential to cause groundwater pollution will probably be addressed in evaluating the agricultural uses of imidacloprid If it is found that in some areas the soil column permeability and other characteristics are such that there is potential for groundwater pollution, then urban stormwater runoff water-quality managers may need to evaluate whether the imidacloprid in urban stormwater runoff could lead to groundwater pollution in the urban area Of particular concern are detention ponds and other vegetated areas that tend to promote groundwater infiltration as well as groundwater infiltration basins. We (1998) have discussed the importance of monitoring groundwater potentially impacted by stormwater infiltration basins to determine if the infiltrated groundwater contains chemical constituents that can pollute groundwater.

Another issue concerning the use of imidacloprid is that it breaks down into several chemicals that have not been properly evaluated with respect to causing aquatic life toxicity. The evaluation of a pesticide for adverse impacts to non-target organisms should include incubation studies where the toxicity of the pesticide to the standard test organisms is evaluated after about one week, one month, and several months of appropriate incubation under aerobic and anaerobic conditions.

This approach would screen for highly toxic breakdown products.

Urban Pesticide Committee

Several years ago, the San Francisco Regional Water Quality Control Board and the Central Valley Regional Water Quality Control Board staffs organized the Urban Pesticide Committee (UPC). The UPC addresses a broad range of issues related to pesticides and water quality In addition to being an information clearinghouse, the UPC serves as a stakeholder forum for development of the Diazinon and Pesticide-Related Toxicity in Bay Area Urban Creeks Water Quality Attainment Strategy (WQAS) and Total Maximum Daily Load, and as a mechanism for tracking WQAS implementation. The UPC holds a meeting every two months in Oakland CA, where urban pesticide water-quality-related issues are discussed It is possible to participate in these meetings via conference call More information is available online (see sidebar).

Overall Status of Replacement Pesticides Impacts Evaluation

The sale of diazinon and chlorpyrifos for residential use should end in about two years when the existing residential stocks are used, greatly reducing and possibly eliminating aquatic life toxicity to *Ceriodaphnia* due to diazinon and chlorpyrifos in urban stormwater. However the significant deficiencies in the OPP regulatory process for registration of pesticides—where pesticides highly toxic to one or more forms of aquatic life receive labels that allow for use without evaluating whether stormwater runoff and fugitive water releases for the areas of application—can cause aquatic life toxicity in the receiving waters for the runoff. Water-quality regulatory agencies and urban stormwater-quality managers must take a proactive approach to evaluating whether new or expanded use of pesticides, such as the pyrethroid-based pesticides being used in large amounts in urban areas as replacement for diazinon and chlorpyrifos are causing aquatic life toxicity in the urban receiving waters for stormwater runoff.

The stormwater NPDES permits that are being issued by the Central Valley Regional Water Quality Control Board and other Regional Boards are a major step in the right direction to becoming proactive to detecting aquatic life toxicity in the receiving water runoff water column NPDES permits that do not require receiving water sediment toxicity are deficient in evaluating the potential impacts of the pyrethroid-based and other pesticides that tend to strongly attach to surfaces and sediments and therefore tend to be adverse to the benthic organism–based food web. Sediment aquatic life toxicity testing using EPA standard benthic organism toxicity tests should be part of the stormwater NPDES required monitoring.

It will be important that urban stormwater managers periodically—at least biannually—survey the large local garden and home pesticide retail sale locations to determine what pesticides are being sold to the public for home use When new or significantly expanded sale of pesticides occurs, a preliminary evaluation of the potential to cause toxicity in urban stormwater runoff based on the use of the OPP Ecotoxicity Database should be conducted. If the LC50 for the pesticide for *Daphnia magna*, mysid, and freshwater and marine larval fish is greater than about 3,000 nanograms per liter, and if the pesticide is used at application rates similar to diazinon, it is unlikely that the pesticide will cause water column aquatic life toxicity in receiving waters. However, studies will need to be conducted to determine if the pesticide transformation products can cause aquatic life toxicity in stormwater runoff. At this time there is insufficient information on the toxicity of pesticides that tend to accumulate in aquatic sediments to establish a screening level LC50.

If the pesticide has a K_{OC} or sorption coefficient similar to the currently used pyrethroid-based pesticides, then there is need to evaluate if it can cause aquatic life toxicity in receiving water sediments through the use of sediment toxicity tests. If sediment toxicity is found in the areas where sediments from stormwater runoff tend to accumulate in the receiving waters for urban stormwater runoff, then benthic organism bioassessment studies need to be conducted relative to reference areas with similar benthic organism habitat that have not received the pesticide to determine if the benthic organism assemblages are impacted by the toxicants in the stormwater runoff.

It is also important to evaluate whether highly mobile pesticides can cause groundwater pollution through infiltration This will require groundwater monitoring near areas where groundwater infiltration occurs, especially near groundwater infiltration–based BMPs.

In order to screen for current water-quality problems caused by organochlorine pesticides such as DDT and its transformation products, chlordane, and others, representative samples of fish should be collected from the stream and analyzed of these pesticides in the edible tissue If only small fish are available, then whole fish can be used. The analytical results should be examined relative to current EPA and any state/local guidelines for protection of human health If there are individuals that use fish from the stream for food at a rate greater than the guideline-assumed value, then the guideline should be adjusted for the fish consumption rate applicable to the water body.

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This article is based on an expanded discussion of urban pesticide–caused aquatic life toxicity provided in the Stormwater Runoff Water Quality Newsletter. Volume 8 1/2 (Jones-Lee 2005), which is available at http://www.gfredlee.com/newsindex.htm

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